



# Stereochemistry of oxidative addition reactions of cycloneophyl complexes of Platinum(II): A methylene insertion reaction from dichloromethane

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## ABSTRACT

Unusual features are observed in studies of oxidative addition to cycloneophylplatinum(II) complexes [Pt(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(NN)], **2**, NN = 3,4,7,8-tetramethyl-1,10-phenanthroline (phen\*) or **3**, NN = 4,4'-di-*t*-butyl-2,2'-bipyridine (bubipy). The oxidative addition of 4-nitrobenzyl bromide to **2** or of HgCl<sub>2</sub> to **3** occurs with *cis* stereochemistry to give [PtBr(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(phen\*)] or [PtCl(HgCl)(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(bubipy)], whereas similar reactions with dimethylplatinum(II) complexes occur with *trans* stereochemistry. The reaction of **2** with CH<sub>2</sub>Cl<sub>2</sub> occurs, with formal insertion of methylene into the arylplatinum bond, to give [PtCl<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)(phen\*)], the first time such a reaction has been observed with the reagent CH<sub>2</sub>Cl<sub>2</sub>. Hydrogen peroxide reacts with **2** to give oxidative addition with *trans* stereochemistry to give [Pt(OH)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(phen\*)] and reaction with chlorinated solvent then gives [PtCl(OH)(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(phen\*)]. Depending on the reaction conditions, the peroxyacid *m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>3</sub>H reacts with **2** to give [Pt(OH)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(phen\*)(*m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>], [Pt(OH)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(phen\*)(Pt(OH)(OH<sub>2</sub>)(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(phen\*))(*m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>3</sub>], or [PtCl{OOC(=O)C<sub>6</sub>H<sub>4</sub>Cl-*m*}(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(phen\*)]. Computational studies indicate that the stereochemistry of oxidative addition may be determined by kinetic or thermodynamic factors in different cases, and that the unique CH<sub>2</sub> insertion reaction with CH<sub>2</sub>Cl<sub>2</sub> occurs by a radical mechanism. X-ray structure determinations are reported for eight of the platinum(IV) complexes.

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## 1. Introduction

The oxidative addition reaction gives one of the most important means of bond activation in catalysis, and it has been studied in great detail [1–3]. The stereochemistry of addition often gives insight into the reaction mechanism. Thus, concerted oxidative addition typically leads to *cis* stereochemistry of addition while stepwise mechanisms usually lead to *trans* stereochemistry under conditions of kinetic control. A typical example is shown in Scheme 1 for stepwise addition, by the polar S<sub>N</sub>2 mechanism, of CD<sub>3</sub>I to [PtMe<sub>2</sub>(2,2'-bipyridine)], **A**, in a donor solvent (S = MeCN, Me<sub>2</sub>CO, MeOH) [4]. A 5-coordinate intermediate **B** can be trapped by solvent (fast) to give **C** or iodide (intermediate rate) to give **D** or isomerize (slow) to give **E** and then **F**, eventually giving a mixture of **D** and **F** with scrambling of CH<sub>3</sub> and CD<sub>3</sub> groups in the product [PtI Me<sub>2</sub>(CD<sub>3</sub>)(2,2'-bipyridine)]. The dihalogenoalkanes CH<sub>2</sub>X<sub>2</sub> can act as methylene transfer reagents, especially in

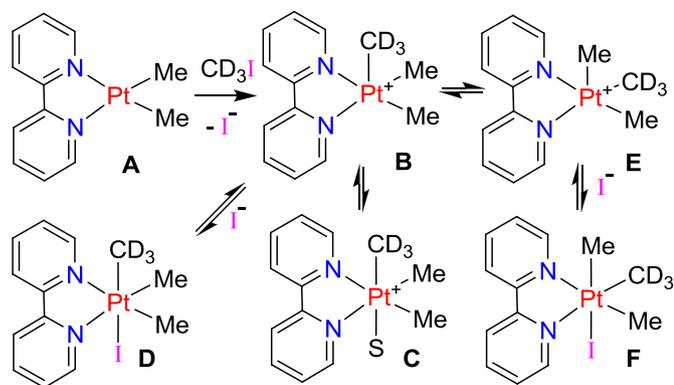
organopalladium chemistry, and mechanisms involving oxidative addition may be involved in some cases [5,6]. This article reports oxidative addition chemistry of the cycloneophylplatinum complexes [Pt(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(NN)], with NN = diimine ligand [7]. It establishes unusual *cis* oxidative addition reactions with benzylic halides or mercury(II) halides, and a reaction in which dichloromethane can act as an effective source of methylene for insertion into the arylplatinum bond.

## 2. Results and discussion

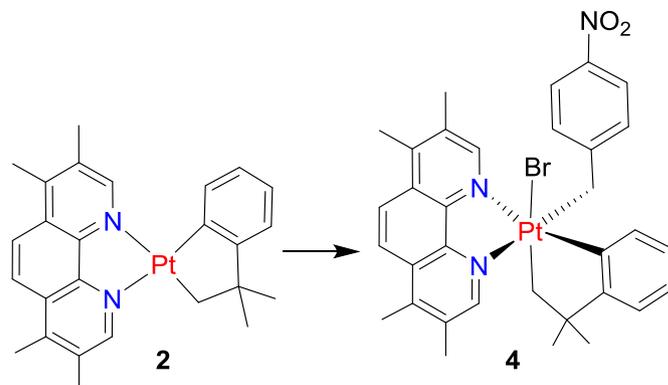
The cycloneophylplatinum(II) complexes with diimine ligands 3,4,7,8-tetramethyl-1,10-phenanthroline (phen\*) or 4,4'-di-*t*-butyl-2,2'-bipyridine (bubipy) were prepared as shown in Scheme 2 [7]. Thus, treatment of the binuclear complex **1** with the appropriate diamine ligand gave the orange complex **2** or **3**. Because these complexes are reactive, they were generally prepared *in situ* and then used in further reactions as described below. The products of oxidative addition typically have no symmetry and the structures were not easily deduced from spectroscopic data, so details are

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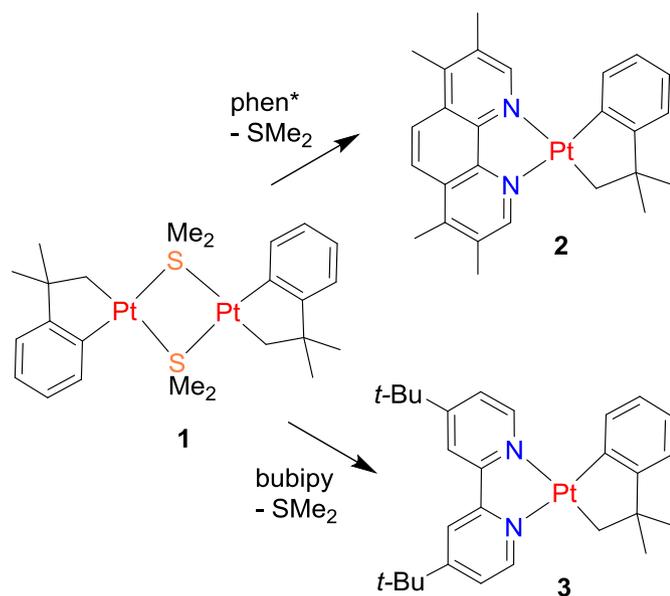
E-mail address: [pudd@uwo.ca](mailto:pudd@uwo.ca) (R.J. Puddephatt).



**Scheme 1.** Mechanism of reaction of  $[\text{PtMe}_2(\text{bipy})]$  with  $\text{CD}_3\text{I}$  ( $S = \text{solvent}$ ).



**Scheme 3.** Oxidative addition of  $\text{BrCH}_2\text{C}_6\text{H}_4\text{-4-NO}_2$  to give complex **4**.



**Scheme 2.** Synthesis of complexes **2** and **3**.

reported only for the complexes which were structurally characterized.

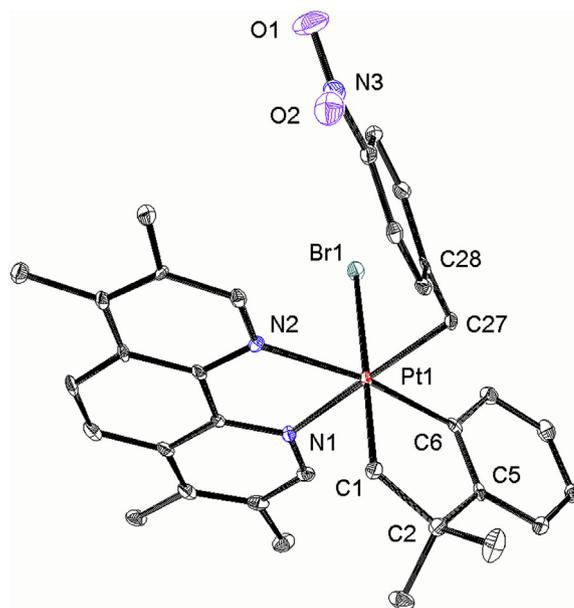
### 2.1. Oxidative addition with 4-nitrobenzyl bromide

The reaction of complex **2** with 4-nitrobenzyl bromide occurred rapidly to give the colorless platinum(IV) complex  $[\text{PtBr}(\text{CH}_2\text{-4-C}_6\text{H}_4\text{NO}_2)(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{phen}^*)]$ , **4**, by *cis* oxidative addition (Scheme 3). When the reaction was carried out in acetone solution, the product **4** precipitated from solution and it was characterized by its NMR spectrum as a single isomer before and after recrystallization from dichloromethane/pentane. The unexpected feature of the reaction is the *cis* stereochemistry of the reaction, since oxidative addition of benzyl halide derivatives to dimethylplatinum(II) complexes occur with *trans* stereochemistry and such reactions have been used in synthesis of a wide range of functional organoplatinum(IV) complexes, including dendrimers and supramolecular polymers [2,3,8–11]. There are few prior examples of selective *cis* oxidative addition of benzyl halides and, as with complex **2**, they involve cyclometallated derivatives [2,3,12,13].

The structure of the chiral complex **4** was determined as both the unsolvated complex and as the dichloromethane solvate **4**. $\text{CH}_2\text{Cl}_2$ . The molecular structures are almost identical, and the

structure of **4** as the dichloromethane solvate is shown in Fig. 1. In each crystalline form, the 4-nitrobenzyl group is oriented towards the adjacent nitrogen donor with torsion angle  $\text{N}(2)\text{Pt}(1)\text{C}(27)\text{C}(28) = 0.8^\circ$  in **4** (Fig. 1) and  $2.1^\circ$  in **4**. $\text{CH}_2\text{Cl}_2$ . There is one significant difference between the two structural forms. The dichloromethane solvate crystallizes in space group  $P2_1/c$  and so contains equal amounts of the two enantiomers, while the unsolvated form crystallizes in space group  $P2_12_12_1$  and so all molecules in the crystal have the same chirality at the asymmetric platinum(IV) center by spontaneous resolution.

In the  $^1\text{H}$  NMR spectrum of complex **4**, each  $\text{CH}_2$  group (benzyl and cycloneophyl) appears as an “AB” multiplet, as expected for the asymmetric structure, while the *ortho* and *meta* protons of the 4-nitrobenzyl group each give a single resonance, indicating fast rotation about the  $\text{CH}_2\text{-C}$  bond. The  $\text{CH}_2$  protons of the neophyl group were at  $\delta(^1\text{H})$  2.85 [ $^2J(\text{PtH}) = 72$  Hz] and 1.85 [ $^2J(\text{PtH}) = 97$  Hz] and those for the benzyl group were at  $\delta(^1\text{H})$  3.99 [ $^2J(\text{PtH}) = 105$  Hz] and 3.94 [ $^2J(\text{PtH}) = 100$  Hz]. In each case the geminal coupling was  $^2J(\text{HH}) = 9$  Hz.



**Fig. 1.** The structure of complex **4**, as  $\text{CH}_2\text{Cl}_2$  solvate. Selected bond parameters:  $\text{Pt}(1)\text{C}(1)$  2.059(5),  $\text{Pt}(1)\text{C}(6)$  2.018(5),  $\text{Pt}(1)\text{C}(27)$  2.089(5),  $\text{Pt}(1)\text{N}(1)$  2.141(4),  $\text{Pt}(1)\text{N}(2)$  2.210(4),  $\text{Pt}(1)\text{Br}(1)$  2.5957(7) Å;  $\text{C}(6)\text{Pt}(1)\text{C}(1)$  82.92(19),  $\text{N}(1)\text{Pt}(1)\text{N}(2)$  76.03(16) $^\circ$ ;  $\text{N}(2)\text{Pt}(1)\text{C}(27)\text{C}(28)$   $0.8^\circ$ .

## 2.2. Oxidative carbene insertion with dichloromethane

An orange solution of complex **2** in dichloromethane slowly became colorless over a period of days and crystals of complex **5** were isolated (Scheme 4). A similar reaction in  $\text{CD}_2\text{Cl}_2$  was monitored by  $^1\text{H}$  NMR spectroscopy and slowly formed **5-d<sub>2</sub>** in high yield over a period of three days. No long-lived intermediates were detected in this reaction. Complex **5** has no symmetry and the two  $\text{CH}_2$  groups again appeared as AB multiplets in the  $^1\text{H}$  NMR spectra, with the  $\text{CH}_2\text{CMe}_2$  protons at  $\delta(^1\text{H}) = 2.88$ ,  $^2J(\text{PtH}) = 74$  Hz, and  $1.88$ ,  $^2J(\text{PtH}) = 98$  Hz, and the  $\text{CH}_2\text{C}_6\text{H}_4$  protons (absent for **5-d<sub>2</sub>**) at  $\delta(^1\text{H}) = 4.99$ ,  $^2J(\text{PtH}) = 95$  Hz, and  $4.37$ ,  $^2J(\text{PtH}) = 31$  Hz.

The structure of complex **5** is shown in Fig. 2. The two chlorine atoms and the  $\text{CH}_2$  group derived from dichloromethane are in a meridional arrangement at the octahedral platinum(IV) center, with the two chloride ligands mutually *cis*. There is now a 6-membered  $\text{PtCH}_2\text{CMe}_2\text{C}_6\text{H}_4\text{CH}_2$  ring, which adopts a twist-boat conformation and which is formed by formal insertion of a  $\text{CH}_2$  group into the aryl-platinum bond of complex **2**.

The closest analogy to the above chemistry is in the reactivity of the anionic palladium(II) complex **G** (NNN = tripyrazolylborate) with dihalogenomethane derivatives to give **H** or **I** (Scheme 5) [6]. The reaction with dibromomethane or diiodomethane gave the carbene insertion product (**I** when  $\text{X} = \text{Br}$ ), analogous to the platinum complex **5**, but dichloromethane gave only the oxidative addition product **H**. The reaction to give **5** by formal methylene group insertion from dichloromethane therefore appears to be unique [5,6]. Many organoplatinum(II) complexes with N-donor ligands react with dichloromethane, but typically only to give isomeric mixtures of chloromethylplatinum(IV) complexes by simple oxidative addition [3,8,14,15].

## 2.3. Oxidative addition with mercury(II) chloride.

Mercury(II) chloride reacted rapidly with complex **3** to give the Pt-Hg bonded platinum(IV) complex  $[\text{PtCl}(\text{HgCl})(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{-bubipy})]$ , **6** (Scheme 6). Complex **6** was formed as a single isomer, with the characteristic  $\text{CH}^a\text{H}^b$  resonances in the  $^1\text{H}$  NMR spectrum at  $\delta(^1\text{H})$  3.09,  $^2J(\text{PtH}) = 65$  Hz, and 2.22,  $^2J(\text{PtH}) = 106$  Hz, each with  $^2J(\text{H}^a\text{H}^b) = 9$  Hz.

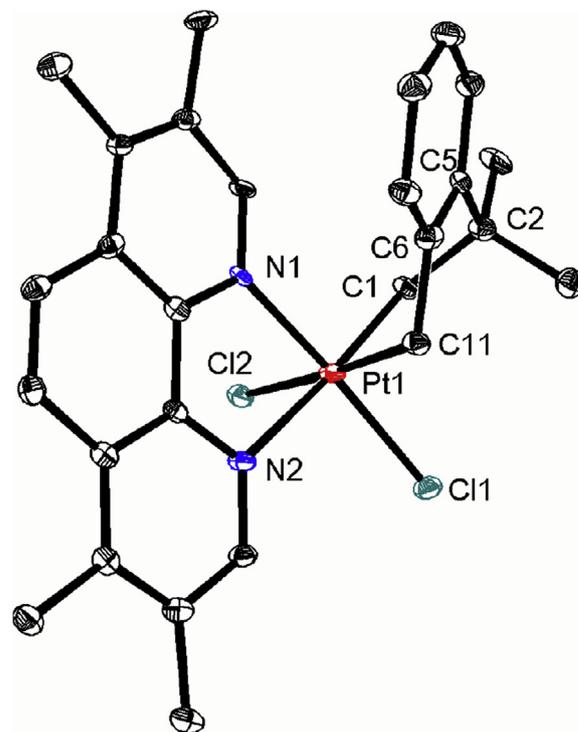
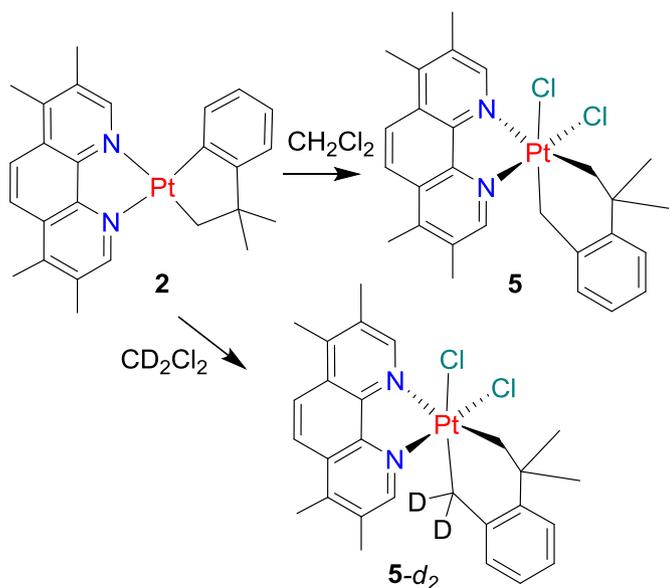
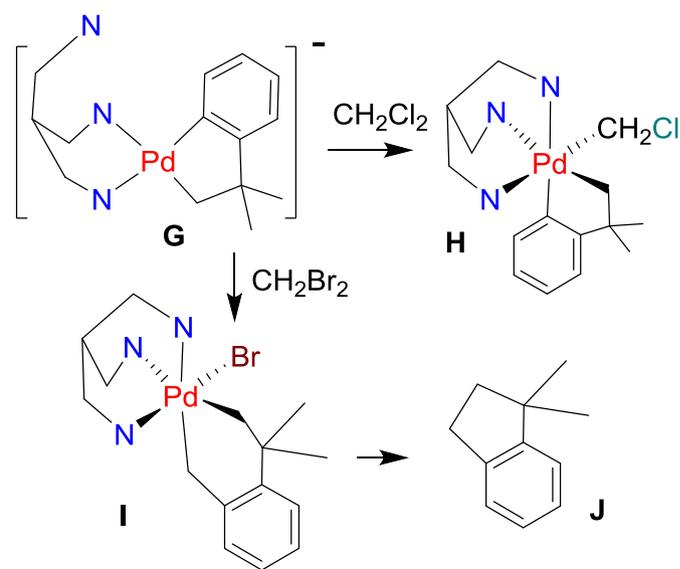


Fig. 2. The structure of complex **5**. Selected bond parameters: Pt(1)N(1) 2.050(5), Pt(1)C(1) 2.058(7), Pt(1)C(11) 2.079(6), Pt(1)N(2) 2.152(6), Pt(1)Cl(1) 2.3019(17), Pt(1)Cl(2) 2.4819(17) Å; C(1)Pt(1)C(11) 90.1(3), N(1)Pt(1)N(2) 79.6(2)°.

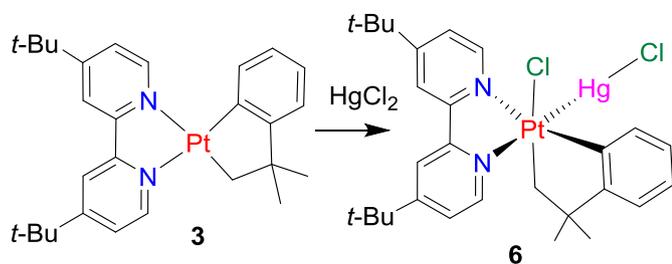
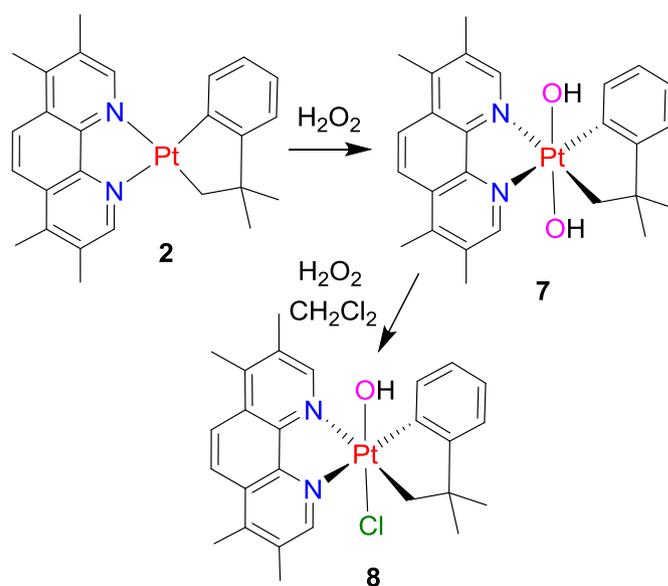
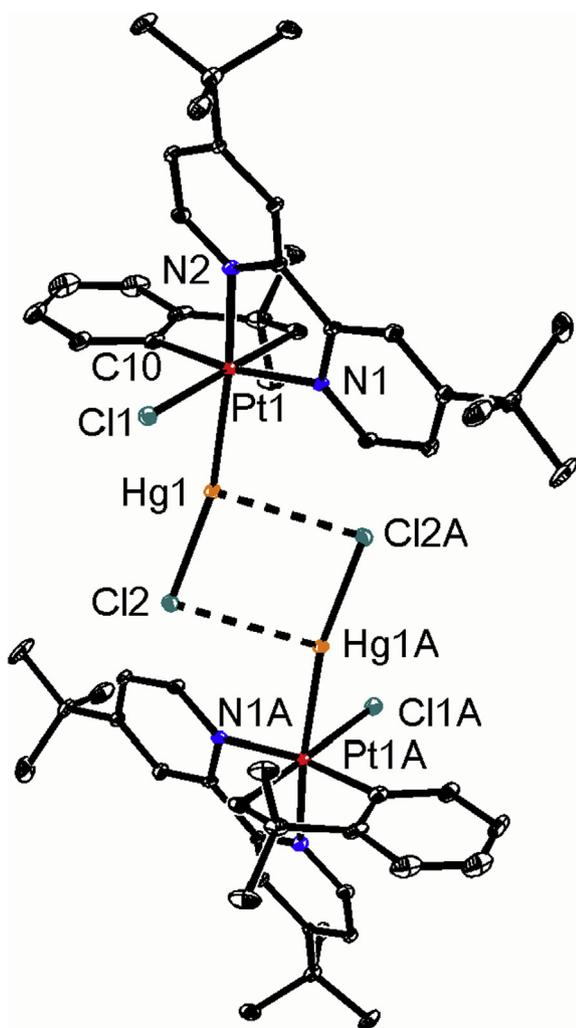
The structure of complex **6** is shown in Fig. 3. The most noteworthy feature is the *cis* orientation of the Cl and  $\text{HgCl}$  ligands, since all analogous complexes formed by oxidative addition of mercury(II) halides to platinum(II) complexes have the *trans* stereochemistry [16]. The complex forms a supramolecular dimer by forming complementary intermolecular  $\text{Hg}\cdots\text{Cl}$  bonds with  $\text{Hg}(1)\cdots\text{Cl}(2\text{A}) = \text{Hg}(1\text{A})\cdots\text{Cl}(2) = 3.109$  Å. The two molecules in Fig. 3 are related by inversion symmetry, so they form a racemic pair.



Scheme 4. The synthesis of complexes **5** and **5-d<sub>2</sub>**.



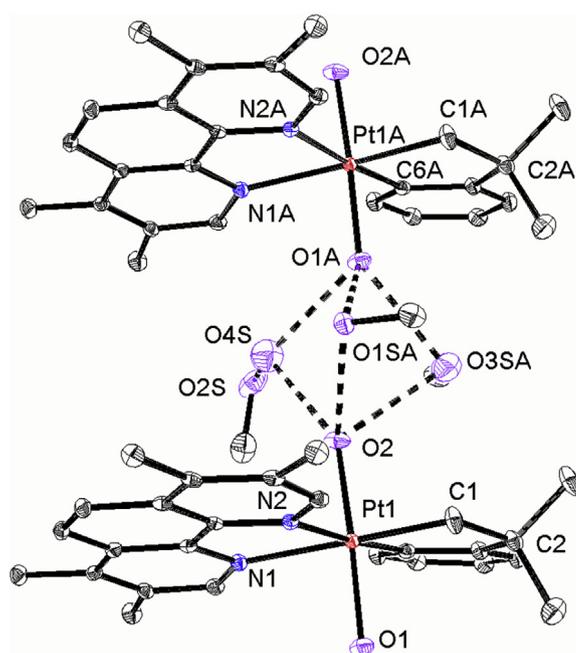
Scheme 5. Reactions of palladium(II) complexes with dihalogenomethanes [6].

Scheme 6. Reaction of **3** with  $\text{HgCl}_2$ .Scheme 7. Reactions of complex **2** with hydrogen peroxide.

**Fig. 3.** The structure of complex **6**. Selected bond parameters:  $\text{Hg}(1)\text{Pt}(1)$  2.5107(5),  $\text{Hg}(1)\text{Cl}(2)$  2.3815(13),  $\text{Pt}(1)\text{Cl}(1)$  2.4682(14),  $\text{Pt}(1)\text{C}(10)$  2.007(5),  $\text{Pt}(1)\text{N}(1)$  2.111(4),  $\text{Pt}(1)\text{N}(2)$  2.109(4) Å;  $\text{Cl}(2)\text{Hg}(1)\text{Pt}(1)$  165.93(3),  $\text{C}(1)\text{Pt}(1)\text{C}(10)$  82.6(2),  $\text{N}(1)\text{Pt}(1)\text{N}(2)$  77.14(16)°. Symmetry related atoms: x, y, z; 1-x, 1-y, 1-z.

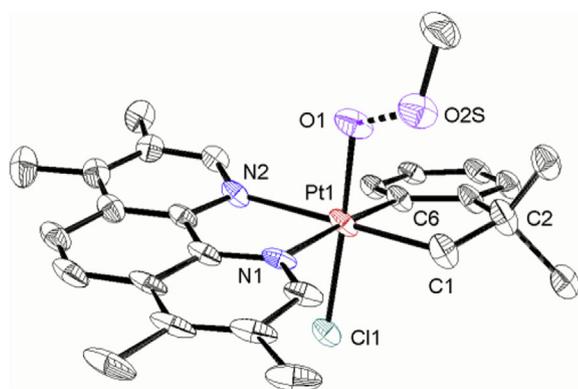
#### 2.4. Oxidative addition with hydrogen peroxide.

Two new complexes were isolated by reaction of complex **2** with aqueous hydrogen peroxide (Scheme 7). The complex  $[\text{Pt}(\text{OH})_2(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{phen}^*)]$ , **7**, was the initial product and it was successfully crystallized from acetone/methanol/pentane as the solvate  $7 \cdot \text{H}_2\text{O} \cdot 0.3\text{MeOH}$ , whose structure is shown in Fig. 4. It is formed by *trans* oxidative addition of the O–O bond of  $\text{H}_2\text{O}_2$ . This is the usual stereochemistry of oxidative addition of  $\text{H}_2\text{O}_2$  [17], with



**Fig. 4.** The structure of solvated complex  $7 \cdot \text{H}_2\text{O} \cdot 0.3\text{MeOH}$ . Selected bond parameters:  $\text{Pt}(1)\text{O}(1)$  1.997(5),  $\text{Pt}(1)\text{O}(2)$  1.952(5),  $\text{Pt}(1)\text{C}(1)$  2.047(6),  $\text{Pt}(1)\text{C}(6)$  2.006(6),  $\text{Pt}(1)\text{N}(1)$  2.229(5),  $\text{Pt}(1)\text{N}(2)$  2.162(5) Å;  $\text{C}(6)\text{Pt}(1)\text{C}(1)$  81.0(3),  $\text{N}(2)\text{Pt}(1)\text{N}(1)$  75.6(2)°.

*cis* stereochemistry only observed when favored by intramolecular hydrogen bonding effects [18]. When complex **7** was crystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , a reaction with solvent occurred to give complex **8** by chloride for hydroxide ligand exchange [19]. The structure of complex **8** as the methanol solvate is shown in Fig. 5, and it also has the *trans* stereochemistry. This selective *trans* oxidative addition contrasts with the *cis* selectivity exhibited in the formation of **4** and **6** (Figs. 1 and 3). The PtOH groups in **7** and **8** are both involved in hydrogen bonding to solvate molecules. For complex **7** this leads to formation of a supramolecular polymeric structure involving head-to-tail association mediated by both  $\text{H}_2\text{O}$  and MeOH solvate molecules (Fig. 4). Complex **7** has an effective plane of symmetry

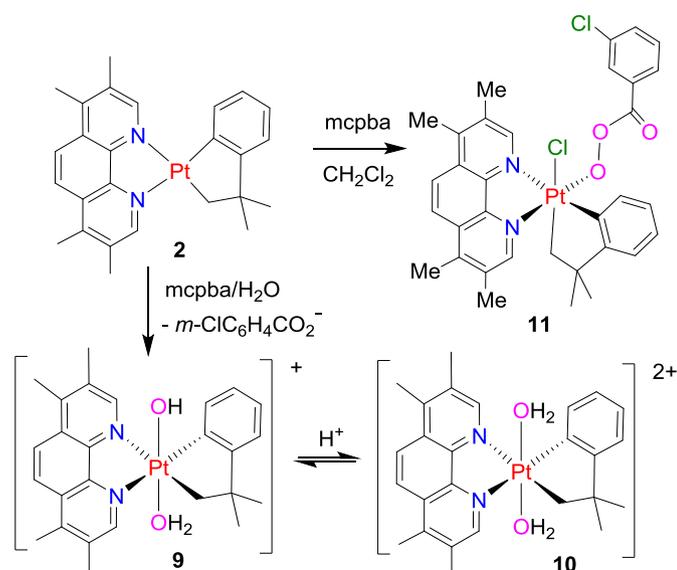


**Fig. 5.** The structure of complex **8**, as the methanol solvate. Selected bond parameters: Pt(1)C(1) 2.043(10), Pt(1)C(6) 2.022(9), Pt(1)O(1) 2.027(7), Pt(1)N(1) 2.145(7), Pt(1)N(2) 2.203(8), Pt(1)Cl(1) 2.327(3) Å; C(1)Pt(1)C(6) 80.8(4), N(1)Pt(1)N(2) 75.7(3)°.

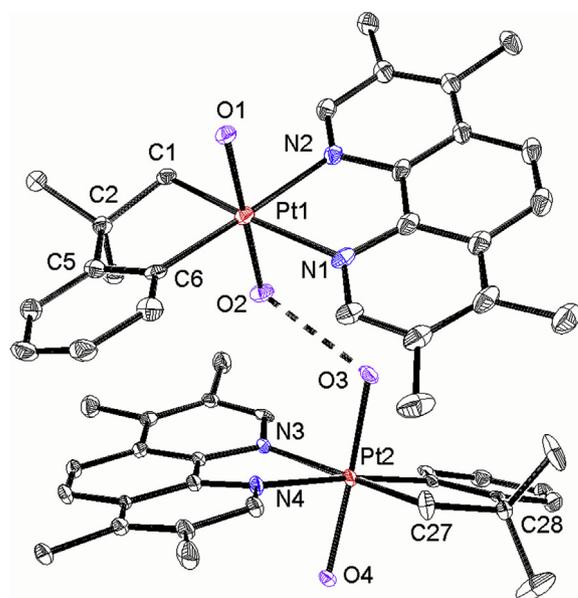
containing the PtN<sub>2</sub>C<sub>2</sub> unit whereas complex **8** does not. This difference is clear in the <sup>1</sup>H NMR spectra, in which the CH<sub>2</sub> protons of the cycloneophyl group are equivalent in complex **7** [ $\delta$ (CH<sub>2</sub>) 3.88, <sup>2</sup>J(PtH) = 81 Hz] but non-equivalent in complex **8** [ $\delta$ (CH<sub>2</sub>) 4.15, <sup>2</sup>J(PtH) = 80 Hz; 3.94, <sup>2</sup>J(PtH) = 94 Hz; each with <sup>2</sup>J(HH) = 8 Hz].

### 2.5. Oxidative addition with *m*-chloroperoxybenzoic acid, mcpcb

The oxidation of complex **2** with mcpcb is shown in Scheme 8. The usual S<sub>N</sub>2 mechanism is expected to give an intermediate [Pt(OH)(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(phen\*)]<sup>+</sup>(*m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sup>-</sup>, which could then be trapped by coordination of the *m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup> anion, by solvent, by adventitious water or by mcpcb. When the reaction was carried out by addition of mcpcb to complex **2** in acetone solution, trapping by water occurred to give **9** and then by further protonation to give **10** as the *m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup> salt. Recrystallization of this complex then occurred with partial deprotonation to give the complex **9.10**.(*m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>3</sub>, whose structure is shown in Fig. 6. In contrast, when the reaction was carried out by addition of complex **2** to excess mcpcb in dichloromethane solution, it seems that trapping by the *m*-chloroperoxybenzoate anion occurred, followed by OH/Cl exchange by reaction with solvent [19], to give complex **11** (Scheme 8), whose structure is shown in Fig. 7.



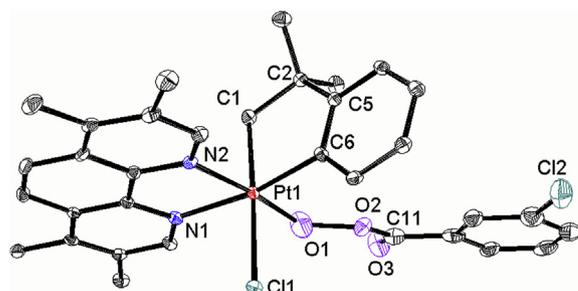
**Scheme 8.** Oxidation of complex **2** with *m*-ClC<sub>6</sub>H<sub>4</sub>C(=O)OOH, mcpcb.



**Fig. 6.** The structure of [Pt(OH)(OH<sub>2</sub>)(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(phen\*))]<sub>2</sub>[Pt(OH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(phen\*))](*m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>3</sub>, **9.10**.(*m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>3</sub>. Selected bond parameters: Pt(1)O(1) 1.971(6), Pt(1)O(2) 2.016(6), Pt(1)C(1) 2.035(9), Pt(1)C(6) 2.036(10), Pt(1)N(1) 2.221(8), Pt(1)N(2) 2.158(8), Pt(2)O(3) 2.005(6), Pt(2)O(4) 2.000(6), Pt(2)C(27) 2.036(10), Pt(2)C(32) 2.016(9), Pt(2)N(3) 2.194(8), Pt(2)N(4) 2.176(7) Å; C(1)Pt(1)C(6) 80.1(4), N(2)Pt(1)N(1) 75.9(3), C(32)Pt(2)C(27) 83.1(4), N(4)Pt(2)N(3) 75.8(3)°.

In the structure of **9.10**.(*m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>3</sub> shown in Fig. 6, the bond parameters associated with the two platinum(IV) centers are similar, with both having the *trans* stereochemistry of the PtO<sub>2</sub> atoms. The distance O(2)⋯O(3) of 2.57 Å is indicative of a strong hydrogen bond, and the complex may be thought of as containing two units of **9** with the two PtOH groups bridged by a proton. The complex was refined with the Pt(1) center as **10** and the Pt(2) center as **9**, but this is arbitrary since the H-atoms were not located directly. The <sup>1</sup>H NMR spectra of complexes **7**, **10** and **9.10** were very similar, each having apparent C<sub>s</sub> symmetry, and exhibiting single resonances for the CH<sub>2</sub> protons and for the CMe<sub>2</sub> protons of the cycloneophyl groups. This indicates that rapid reversible proton addition and loss occurs in solution, to give effective equivalence of OH and OH<sub>2</sub> groups in the unsymmetrical complex **9**.

Complex **11** appears to be the first example of a peroxyacyl complex of platinum(IV), though peroxyacylplatinum(II) complexes [20] and other types of peroxyplatinum(IV) complexes [17,21,22] are known. Complex **11** (Fig. 7) is formed by formal *cis* oxidative addition to complex **2**, in contrast to the *trans* stereochemistry (Figs. 4–6) of other compounds **7–10** formed by



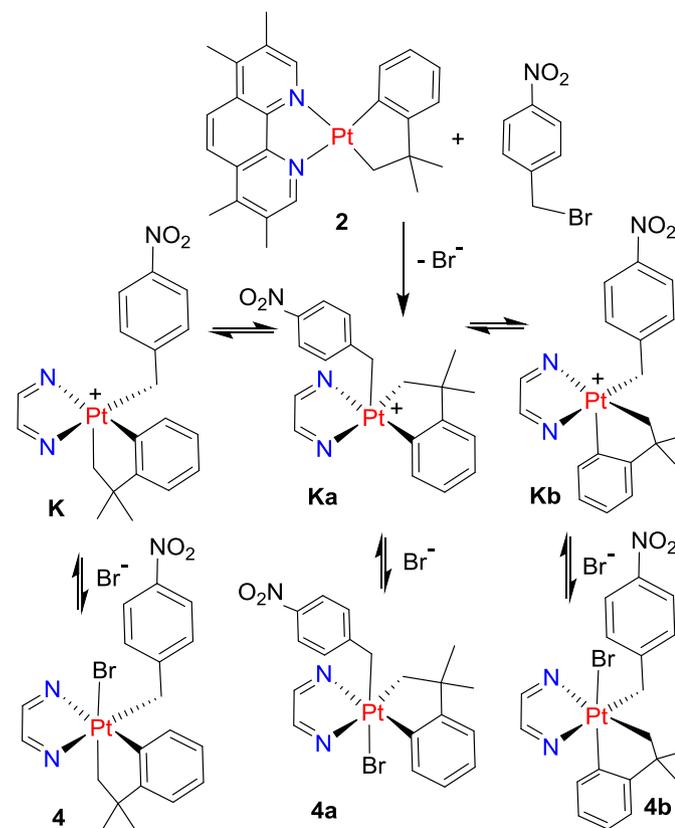
**Fig. 7.** The structure of complex **11**. Selected bond parameters: Pt(1)C(1) 2.061(5), Pt(1)C(6) 2.008(5), Pt(1)O(1) 2.047(5), Pt(1)N(1) 2.147(4), Pt(1)N(2) 2.124(4), Pt(1)Cl(1) 2.464(3), O(1)O(2) 1.525(6) Å; C(6)Pt(1)C(1) 82.27(18), N(2)Pt(1)N(1) 77.94(15)°.

peroxide oxidation. The absence of symmetry in complex **11** is illustrated in the  $^1\text{H}$  NMR spectrum, which contains two resonances for the  $\text{CH}_2$  protons of the cycloneophyl group [ $\delta(^1\text{H})$  4.18,  $^2J(\text{PtH}) = 84$  Hz; 3.95,  $^2J(\text{PtH}) = 80$  Hz, each with  $^2J(\text{HH}) = 7$  Hz].

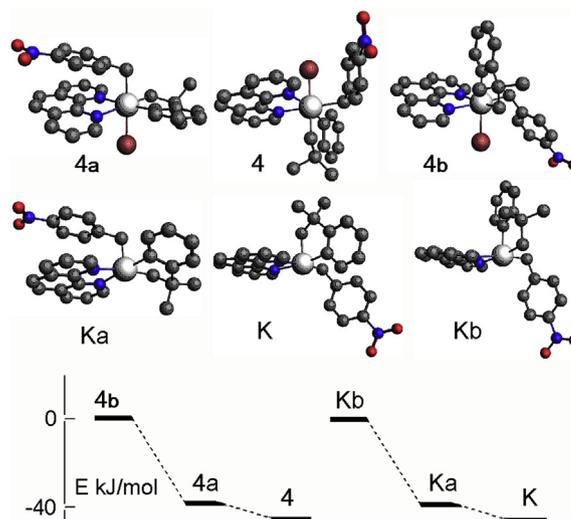
## 2.6. Computational studies

The above studies have established two unanticipated outcomes arising from oxidative addition to the cycloneophylplatinum(II) complex **2** or **3**, and DFT calculations (see experimental for details) were carried out on selected systems to provide insight.

Several of the reactions that were expected to occur by stepwise mechanisms to give products with *trans* stereochemistry were found to occur by *cis* oxidative addition. The reaction of 4-nitrobenzyl bromide with complex **2** is expected to occur by the  $\text{S}_{\text{N}}2$  mechanism, to give initially an ionic intermediate  $[\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{-4-NO}_2)(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{phen}^*)]^+$ , which then gives the product  $[\text{PtBr}(\text{CH}_2\text{C}_6\text{H}_4\text{-4-NO}_2)(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{phen}^*)]$ , according to Scheme 9. The initial intermediate would have stereochemistry **Ka** and bromide coordination would give *trans* addition product **4a** and not the observed product **4**. The 5-coordinate complex **Ka** is expected to be able to isomerize to **K** or **Kb** and then bromide coordination could give **4** or **4b**. The DFT calculations predict that stability follows the series  $\mathbf{4} > \mathbf{4a} > \mathbf{4b}$  and  $\mathbf{K} > \mathbf{Ka} > \mathbf{Kb}$ , and that the energy differences are almost the same for the octahedral complexes and square pyramidal intermediates (Fig. 8). Isomeric complexes **4a** and **4b** appear to be unfavorable with respect to **4** because of steric interactions of the *ortho* proton of the  $\text{C}_6\text{H}_4$  group with the  $\text{phen}^*$  ligand, with the effect partly counteracted in **4a** by favorable  $\pi$ -stacking of the benzyl and  $\text{phen}^*$  aromatic groups. It could be argued that the intermediates **K** and **Kb** might be



**Scheme 9.** Possible intermediates and products for oxidative addition of 4-nitrobenzyl bromide (NN = phen\*).

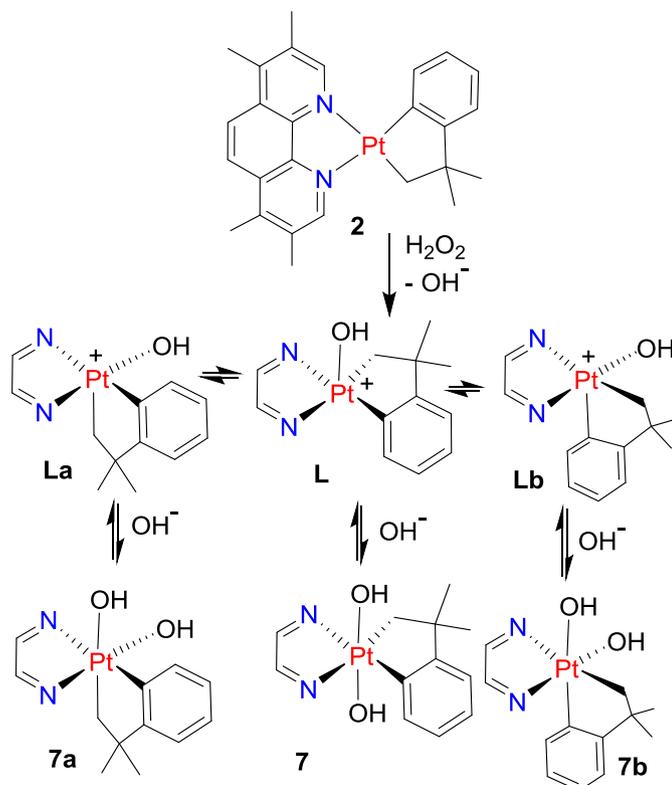


**Fig. 8.** Calculated structures and relative energies (with respect to **4b** and **Kb**) of complexes and intermediates in Scheme 9.

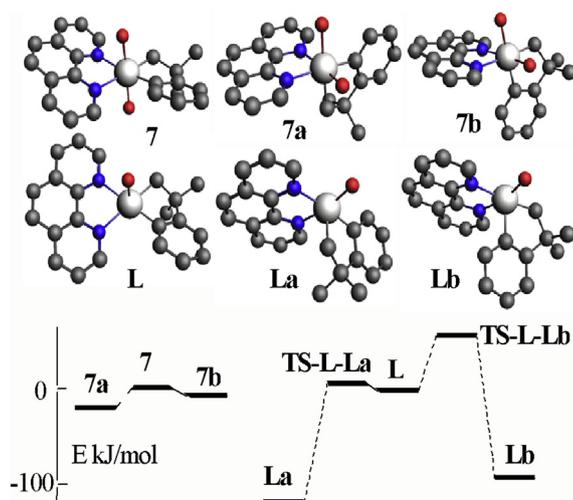
stabilized with respect to **Ka** by formation of a 3-electron benzyl group, but the DFT calculations do not support this interpretation and the benzyl group is predicted to act as a 1-electron ligand in the cationic intermediates.

If the reason for the unusual *cis* oxidative addition is related to steric effects between the cycloneophyl and  $\text{phen}^*$  groups, as predicted above, the new question is why *trans* oxidative addition occurs with hydrogen peroxide in formation of complex **7** (Scheme 7, Fig. 4). A potential reaction sequence is shown in Scheme 10. The initial intermediate would be **L**, which could combine with hydroxide ion to give the observed product **7** or isomerize to **La** or **Lb**, which could then give the *cis* product **7a** or **7b**. The calculated structures and relative energies of these compounds are shown in Fig. 9. Unexpectedly, the *trans* structures **7** and **L** were calculated to be less stable than either of the analogous *cis* products. It should be noted that all of the structurally characterized hydroxoplatinum(IV) complexes are found to exhibit strong hydrogen bonding (Figs. 4–6), and this is not easy to model, so the calculations should be considered with caution. In particular, the energy difference between **7** and the most stable *cis* isomer **7a** is only  $21 \text{ kJ mol}^{-1}$ , and this difference could be reversed by differences in hydrogen bonding and solvation. However, the differences are much greater for the 5-coordinate intermediates, where **La** is calculated to be  $120 \text{ kJ mol}^{-1}$  more stable than **L**. This difference arises because the  $\pi$ -donor hydroxide ligand can stabilize the cationic intermediate by  $p\pi$ - $d\pi$  bonding to the vacant  $6p_z$  orbital of platinum in either of the *cis* structures **La** or **Lb**, but not in **L** [23]. The barrier to isomerization of **L** to **La** is calculated to be only  $12 \text{ kJ mol}^{-1}$ , so the kinetic product by this mechanism would be expected to be the *cis* product **7a**. The simplest explanation is that the oxidative addition by cleavage of the O–O bond of  $\text{H}_2\text{O}_2$  is aided by the synchronous coordination of water in the *trans* position so that the coordinatively unsaturated intermediate **L** is not formed in this reaction.

The second unexpected reaction was the reaction with dichloromethane to give complex **5** (Scheme 4, Fig. 2), and some potential mechanisms were explored by DFT. For the analogous palladium chemistry, two mechanisms were considered, each involving initial oxidative addition to give the bromo analog of **H** (Scheme 5) [6]. One involved reductive elimination to form a Pd(II)  $\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$  group followed by rapid oxidative addition of the C–Br bond to give **H**, while the second involved bromide



**Scheme 10.** Possible intermediates and products of oxidative addition of  $\text{H}_2\text{O}_2$  to complex **2** ( $\text{NN} = \text{phen}^*$ ).



**Fig. 9.** Calculated structures and relative energies (with respect to **7** and **L**) of complexes and intermediates in **Scheme 10**.

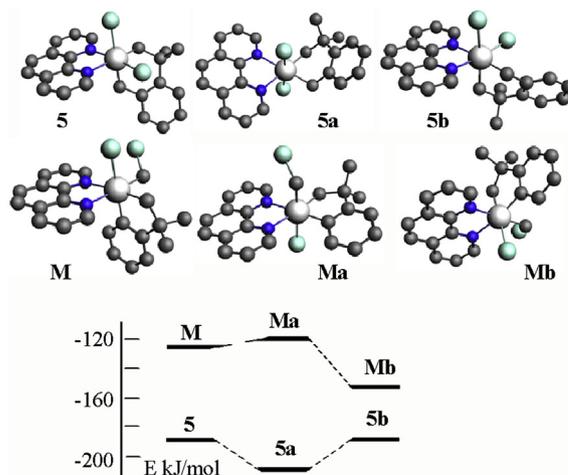
dissociation to give a  $\text{Pd}=\text{CH}_2$  group, followed by insertion of the carbene into the  $\text{Pd}$ -aryl bond to form **H** [6]. These mechanisms are reasonable for the palladium chemistry of **Scheme 5**, but strictly analogous mechanisms are problematic for the platinum chemistry of **Scheme 4**. Oxidative addition of dichloromethane to complex **2** would give isomers of the platinum(IV) complex  $[\text{PtCl}(\text{CH}_2\text{Cl})(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{phen}^*)]$  and this would be expected to be stable to reductive elimination to form an intermediate platinum(II) complex  $[\text{PtCl}(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl})(\text{phen}^*)]$  [14,15] or to ionization of the C-Cl bond to form a carbene complex intermediate

$[\text{PtCl}(\text{=CH}_2)(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{phen}^*)]\text{Cl}$  [6].

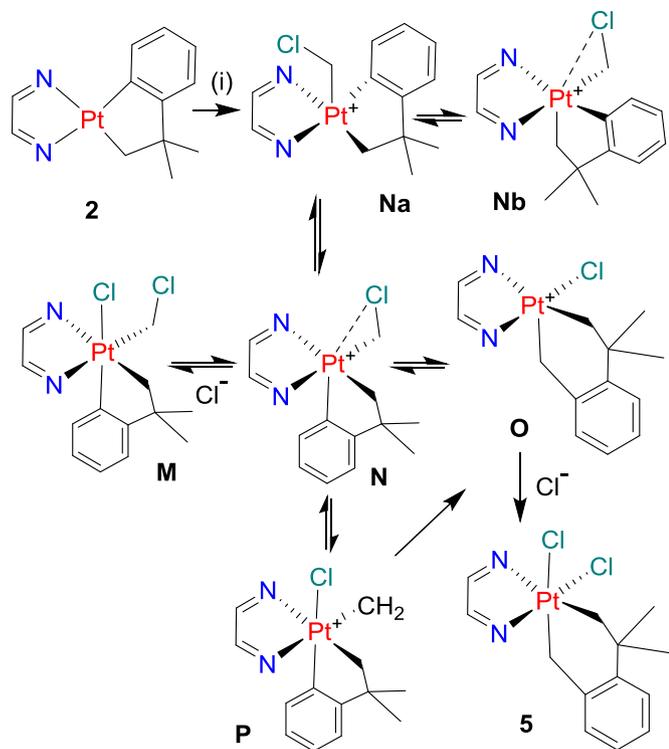
First consider the relative energies of potential isomeric products (**Fig. 10**). The simple oxidative addition would give  $[\text{PtCl}(\text{CH}_2\text{Cl})(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{phen}^*)]$ , which could exist as isomers **M**, **Ma** or **Mb**, while the oxidative addition with methylene insertion would give the corresponding isomers **5**, **5a** or **5b**. The calculations predict that the *trans* isomer **5a** is most stable by  $24 \text{ kJ mol}^{-1}$  over each of the *cis* isomers **5** and **5b**, whereas isomer **5** is the observed product, indicating that **5** is the product of kinetic control. The potential product of *trans* oxidative addition is **Ma**, which is calculated to be less stable than either of the *cis* isomers **M** or **Mb**. This is readily interpreted in terms of the unfavorable interaction between the aryl-phen *o*-hydrogen atoms, which is present in **Ma** but not in any of the other isomers. The chief problem at this point is that no easy direct route from any of the oxidative addition products **M**, **Ma**, **Mb** to the observed product **5** could be found, though the reaction is calculated to be thermodynamically favorable.

Oxidative addition of a C-Cl bond of dichloromethane can take place by the  $\text{S}_{\text{N}}2$  mechanism or by a free radical mechanism (**Schemes 11 and 12**) [3,6,14,24]. Each of these involves 5-coordinate intermediates which might then give  $\text{CH}_2$  insertion. The  $\text{S}_{\text{N}}2$  mechanism (**Scheme 11**) would give **Na**, which could isomerize to **N** or **Nb**, and chloride addition might then give **Ma**, **M** or **Mb**. Similarly, a free radical chain mechanism (**Scheme 12**) would involve initial attack by a  $\text{CH}_2\text{Cl}\cdot$  radical to give **Qa**, which could isomerize to **Q** or **Qb**, and chlorine atom abstraction from  $\text{CH}_2\text{Cl}_2$  would then give **Ma**, **M** or **Mb** and regenerate the  $\text{CH}_2\text{Cl}\cdot$  radical. **Fig. 11** shows the relative energies of these compounds and the transition states for isomerization. In each case, the stability is greater for isomers with equatorial  $\text{CH}_2\text{Cl}$  groups compared to the initially formed isomers with these groups axial. The difference is greatest for the cationic 16-electron intermediates **Nb** and **N** for which a stronger Cl-Pt interaction is predicted to be present. The isomerization is predicted to occur by way of a distorted trigonal bipyramidal intermediate in each case, with a modest barrier ranging from  $43$  to  $76 \text{ kJ mol}^{-1}$ , with the barrier lower for the 17-electron radical complexes than for the 16-electron cations. Simple oxidative addition is not observed but, if it did occur, the *cis* stereochemistry might be expected.

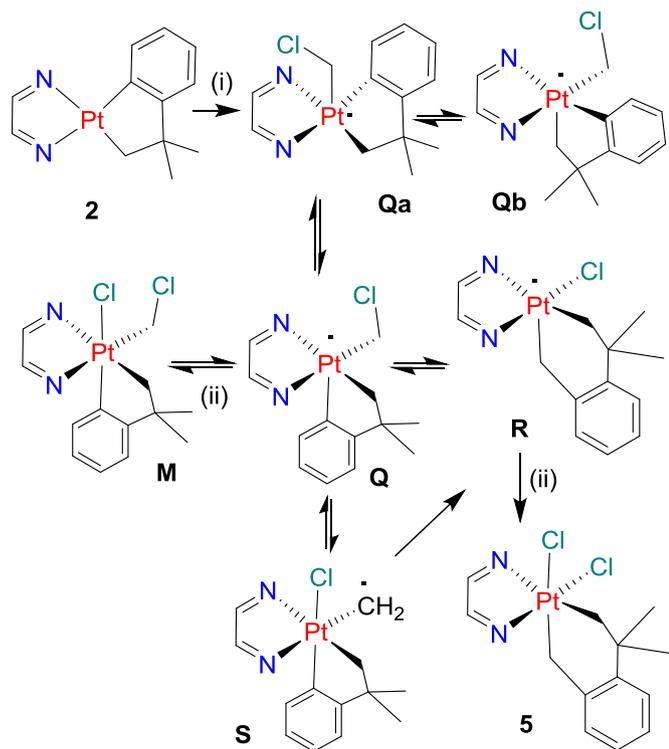
The observed product **5** is most easily formed from the isomer **N** or **Q** and these are calculated to be viable as intermediates. From **N**, the  $\text{CH}_2$  insertion might occur before chloride addition, either



**Fig. 10.** Calculated relative energies (with respect to  $2^* + \text{CH}_2\text{Cl}_2$ ) of potential platinum(IV) products.

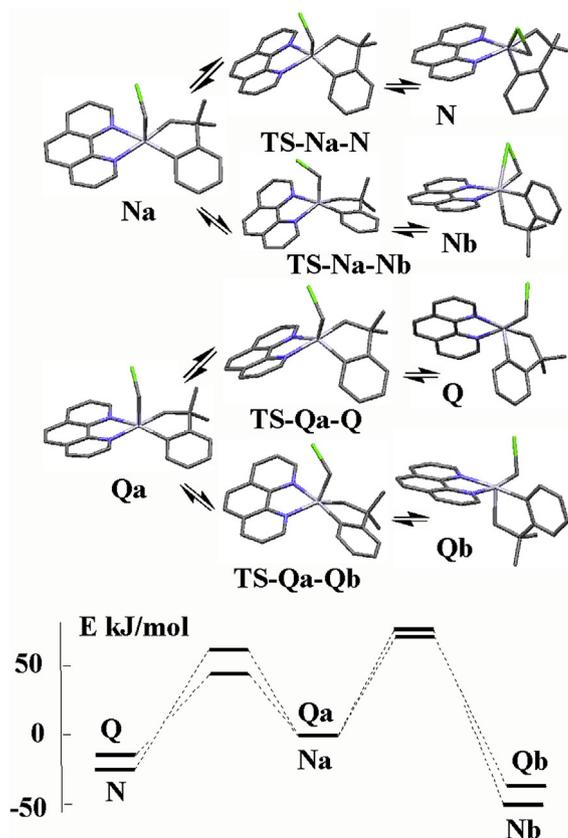


**Scheme 11.** Potential routes to complex **5** via cationic intermediates: NN = phen\*, Reagent (i) = CH<sub>2</sub>Cl<sub>2</sub>, - Cl<sup>-</sup>.



**Scheme 12.** Potential routes to complex **5** via radical intermediates: NN = phen\*, Reagents (i) = CH<sub>2</sub>Cl, (ii) = CH<sub>2</sub>Cl<sub>2</sub>, - CH<sub>2</sub>Cl.

directly or via a carbene complex intermediate **P**, to give **O**; chloride addition could then give the observed product **5** (Scheme 11). No low energy route from any of the isomers **N**, **Na** or **Nb** to the



**Fig. 11.** Calculated structures and energies, relative to **Na** or **Qa**, for isomerization of potential 5-coordinate intermediates.

observed product **5** were found. In particular, no energy minimum for the potential carbene complex **P** was found and, depending on the starting geometry used, spontaneous formation of **N** or **O** was predicted. The lowest energy route from **N** to **O** involved a transition state that resembled one combining C-C (CH<sub>2</sub>Cl-aryl) reductive elimination with C-Cl oxidative addition then occurring spontaneously (Fig. 12). However, the predicted high activation energy appears to rule out this mechanism. The CH<sub>2</sub> insertion from **Q** to give **R** is calculated to occur with a much lower activation energy. It might occur in two steps by way of the carbene intermediate **S**, which is calculated to have mostly the character of a carbon radical PtCH<sub>2</sub>, or more directly (Fig. 12). In such a complex system it is not possible to define a mechanism by DFT calculations, but a radical mechanism is strongly indicated (Scheme 12, Fig. 12).

### 3. Conclusions

The complexes [Pt(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(phen\*)] and [Pt(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(bubipy)] undergo a range of oxidative addition reactions. The stereochemistry of the reaction may be *cis* or *trans*. The unusual *cis* stereochemistry of addition in several cases may partly due to relief of steric interactions between in-plane protons of the diimine and cycloneophyl groups, which will apply to both the 6-coordinate platinum(IV) products and any 5-coordinate platinum(IV) intermediates (Scheme 13). The preference for *cis* stereochemistry is predicted to be enhanced kinetically if a 5-coordinate platinum(IV) intermediate is formed in which the electrophile in the reagent E-X contains a lone pair of electrons in a p<sub>z</sub> orbital that can π-donate to the vacant 6p<sub>z</sub> orbital of platinum (Fig. 9, Scheme 13). When *trans* oxidative addition is observed, for

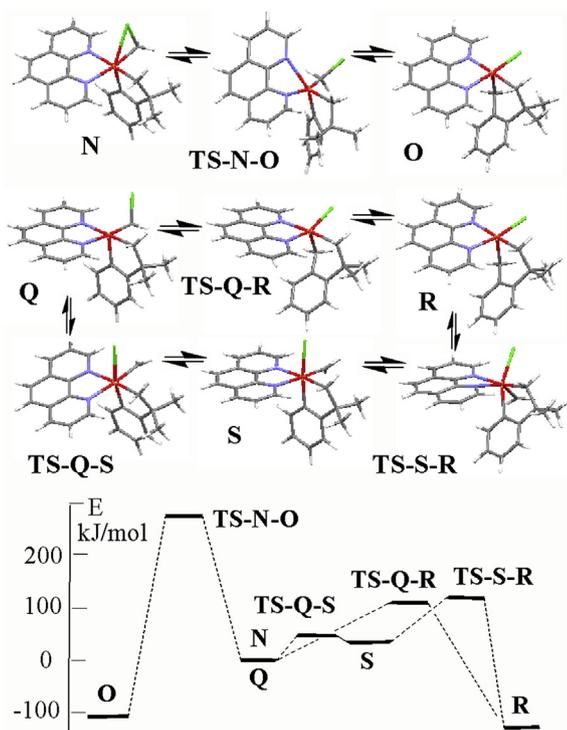


Fig. 12. Calculated structures of possible intermediates and transition states and relative energies with respect to Q or N.

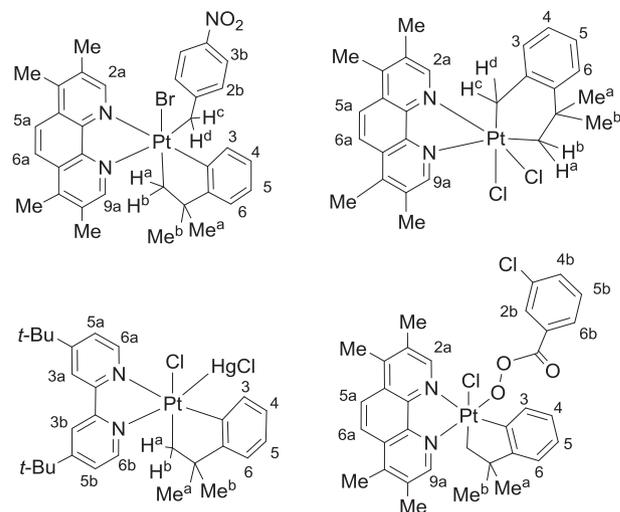


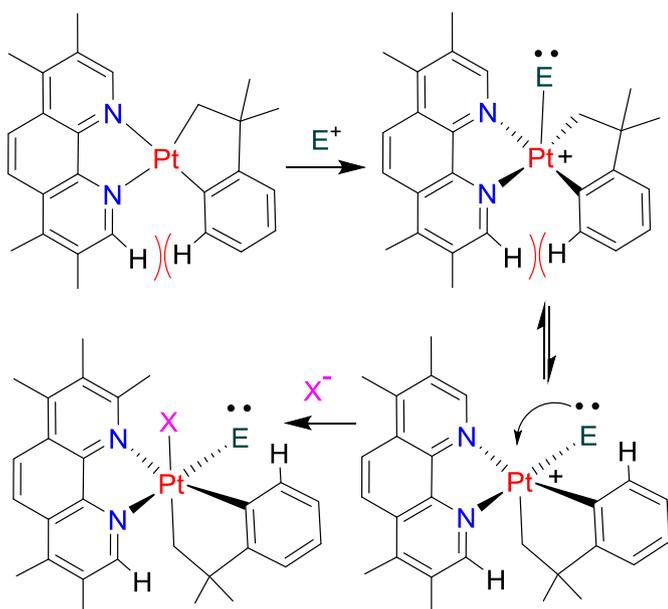
Chart 1. NMR labelling scheme.

#### 4. Experimental

NMR spectra were recorded using Bruker 400 NMR, Inova 400 and Inova 600 spectrometers. The labeling scheme is shown in Chart 1. DFT calculations were carried out by using the Amsterdam Density Functional program based on the BLYP functional, with double-zeta basis set and first-order scalar relativistic corrections. Single-crystal X-ray diffraction measurements were made using a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. Single crystals of the complexes were immersed in paraffin oil and mounted on MiteGen micro-mounts. The structures were solved using direct methods and refined by the full-matrix least-squares procedure of SHELXTL. Crystallographic data are given in the CIF files (CCDC 1901263–1901269). The complexes  $[\text{Pt}_2(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)_2(\mu\text{-SMe}_2)_2]$ ,  $[\text{Pt}(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{phen}^*)]$  and  $[\text{Pt}(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{bu-bipy})]$  were synthesized according to the literature procedure [7].

##### 4.1. $[\text{PtBr}(\text{CH}_2\text{-4-C}_6\text{H}_4\text{NO}_2)(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{phen}^*)]$ , 4

To a sample of complex 2, prepared from 1 (0.084 g, 0.108 mmol) and phen\* (0.051 g, 0.216 mmol) in acetone (5 mL), was added 4-nitrobenzyl bromide (0.46 mmol) in acetone (5 mL). The product formed as a white suspension, which was separated by filtration, washed with acetone ( $2 \times 5$  mL) and pentane ( $2 \times 5$  mL), and recrystallized from  $\text{CH}_2\text{Cl}_2/\text{pentane}$ . Yield: 0.093 g, 55%. Anal. Calcd. for  $\text{C}_{33}\text{H}_{34}\text{BrN}_3\text{O}_2\text{Pt}$ : C, 50.84; H, 4.40; N, 5.39. Found: C, 50.93; H, 4.66; N, 5.49%. NMR in  $\text{CD}_2\text{Cl}_2$ :  $\delta$ ( $^1\text{H}$ ) 8.55 (s, 2H, H $^{5a,6a}$ ), 8.10 (s, 1H,  $^3\text{J}(\text{PtH}) = 19$  Hz, H $^{2a}$ ), 8.02 (d, 1H,  $^3\text{J}(\text{HH}) = 8$  Hz, H $^3$ ), 8.01 (s, 1H,  $^3\text{J}(\text{PtH}) = 12$  Hz, H $^{9a}$ ), 7.92 (d, 2H,  $^3\text{J}(\text{HH}) = 9$  Hz, H $^{2b}$ ), 7.46 (d, 2H,  $^3\text{J}(\text{HH}) = 9$  Hz, H $^{3b}$ ), 7.03 (t, 1H,  $^3\text{J}(\text{HH}) = 8$  Hz, H $^4$ ), 6.89 (t, 1H,  $^3\text{J}(\text{HH}) = 8$  Hz, H $^5$ ), 6.76 (d, 1H,  $^3\text{J}(\text{HH}) = 8$  Hz, H $^6$ ), 3.99 (d, 1H,  $^2\text{J}(\text{PtH}) = 105$  Hz,  $^2\text{J}(\text{HH}) = 9$  Hz, CH $_2^5$ ), 3.94 (d, 1H,  $^2\text{J}(\text{PtH}) = 100$  Hz,  $^2\text{J}(\text{HH}) = 9$  Hz, CH $_2^2$ ), 2.85 (d, 1H,  $^2\text{J}(\text{PtH}) = 72$  Hz,  $^2\text{J}(\text{HH}) = 9$  Hz, CH $_2^3$ ), 2.79 (s, 3H, Me), 2.73 (s, 3H, Me), 2.46 (s, 3H, Me), 2.34 (s, 3H, Me), 1.85 (d, 1H,  $^2\text{J}(\text{PtH}) = 97$  Hz,  $^2\text{J}(\text{HH}) = 9$  Hz, CH $_2^1$ ), 1.18 (s, 3H, Me), 0.67 (s, 3H, Me),  $\delta$ ( $^{13}\text{C}$ ) 161.0, 157.5, 150.5, 149.0, 146.6, 146.5, 145.8, 145.1, 144.4, 138.7, 134.5, 134.3, 134.2, 131.0, 130.4, 130.3, 126.8, 125.2, 124.9, 124.3, 124.2, 123.3, 46.0, 44.0 (CH $_2$ ), 34.8 (Me), 33.7 (Me), 18.5 (Me), 18.3 (Me), 16.1 (CH $_2$ ), 15.5 (Me), 15.4 (Me).



Scheme 13. Factors favoring cis oxidative addition.

example with aqueous hydrogen peroxide, it is suggested that the 5-coordinate intermediate is not formed but that cleavage of the O-O bond of  $\text{H}_2\text{O}_2$  at the platinum center is coincident with coordination of water in the *trans* position. Most of the reactions reported above occur by two electron mechanisms, but the unique methylene insertion reaction probably occurs by a radical mechanism (Scheme 12).

4.2.  $[PtCl_2(CH_2CMe_2C_6H_4CH_2)(phen^*)]$ , 5

A solution of complex **2** was prepared *in situ* by reaction of complex **1** (0.139 g, 0.178 mmol) and ligand phen\* (0.084 g, 0.357 mmol) in  $CH_2Cl_2$  (15 mL). After 3 days the solution was layered with pentane (35 mL) to give colorless block crystals of **6**, which were separated, washed with pentane and dried in vacuum. Yield: 0.083 g, 36%. Monitoring a similar reaction in  $CD_2Cl_2$  solution by  $^1H$  NMR spectroscopy showed slow conversion of complex **2** to complex **3** over 3 days, with no long-lived intermediates detected. Anal. Calcd. for  $C_{27}H_{30}Cl_2N_2Pt$ : C, 50.00; H, 4.66; N, 4.32. Found: C, 49.94; H, 4.57; N, 4.32%. NMR in  $CD_2Cl_2$ :  $\delta(^1H)$  9.51 (s, 1H,  $^3J(PtH) = 11$  Hz,  $H^{2a}$ ), 8.22 (d, 1H,  $^3J(HH) = 9$  Hz,  $H^{5a}$  or  $6a$ ), 8.18 (d, 1H,  $^3J(HH) = 9$  Hz,  $H^{5a}$  or  $6a$ ), 7.99 (d, 1H,  $^3J(HH) = 8$  Hz,  $^4J(PtH) = 38$  Hz,  $H^3$ ), 7.95 (s, 1H,  $^3J(PtH) = 18$  Hz,  $H^{9a}$ ), 7.12 (dd, 1H,  $^3J(HH) = 8$ ,  $^3J(HH) = 8$  Hz,  $H^4$ ), 7.12 (d, 1H,  $^3J(HH) = 8$  Hz,  $H^6$ ), 4.99 (d, 1H,  $^2J(HH) = 8$  Hz,  $^2J(PtH) = 95$  Hz,  $CH_2^c$ ), 4.37 (d, 1H,  $^2J(HH) = 8$  Hz,  $^2J(PtH) = 31$  Hz,  $CH_2^d$ ), 2.88 (d, 1H,  $^2J(HH) = 9$  Hz,  $^2J(PtH) = 74$  Hz,  $CH_2^e$ ), 2.80 (s, 3H, Me), 2.72 (s, 3H, Me), 2.66 (s, 3H, Me), 2.33 (s, 3H, Me), 1.88 (d, 1H,  $^2J(HH) = 9$  Hz,  $^2J(PtH) = 98$  Hz,  $CH_2^f$ ), 1.28 (s, 3H,  $Me^{ab}$ ), 0.84 (s, 3H,  $Me^{ab}$ );  $\delta(^{13}C)$  162.4, 151.5, 150.0, 146.7, 146.5, 145.4, 144.6, 138.0, 134.6, 134.3, 132.5, 130.2, 126.6, 125.5, 125.3, 124.9, 124.4, 124.0, 46.2, 44.3 ( $CH_2$ ), 34.0 (Me), 33.8 (Me), 23.2 ( $CH_2$ ), 18.6 (Me), 18.3 (Me), 15.5 (Me), 15.4 (Me).

4.3.  $[PtCl(HgCl)(CH_2CMe_2C_6H_4)(bubipy)]$ , 6

To a sample of complex **3**, prepared from complex **1** (0.100 g, 0.128 mmol) and ligand bubipy (0.069 g, 0.257 mmol) in acetone (5 mL) was added  $HgCl_2$  (0.070 g, 0.257 mmol) in acetone (2 mL). The solution was stirred for 1 h, the solvent was removed under vacuum, the solid product was washed with  $Et_2O$  ( $2 \times 10$  mL) and pentane ( $2 \times 10$  mL), dried under vacuum, and recrystallized from  $CH_2Cl_2$ /pentane. Yield: 0.154 g, 68%. Anal. Calcd. for  $C_{28}H_{36}Cl_2HgN_2Pt$ : C, 38.78; H, 4.18; N, 3.23. Found: C, 38.51; H, 4.11; N, 3.13%. NMR in  $CD_2Cl_2$ :  $\delta(^1H)$  9.32 (d, 1H,  $^3J(HH) = 6$  Hz,  $^3J(PtH) = 14$  Hz,  $H^{6a}$ ), 8.21 (s, 1H,  $H^{3a,3b}$ ), 8.18 (s, 1H,  $H^{3a,3b}$ ), 7.99 (d, 1H,  $^3J(HH) = 9$  Hz,  $^3J(PtH) = 34$  Hz,  $H^3$ ), 7.74 (d, 1H,  $^3J(HH) = 6$  Hz,  $^3J(PtH) = 24$  Hz,  $H^{6b}$ ), 7.62 (d, 1H,  $^3J(HH) = 6$  Hz,  $H^{5a}$ ), 7.46 (d, 1H,  $^3J(HH) = 6$  Hz,  $H^{5b}$ ), 7.07 (dd, 1H,  $^3J(HH) = 8$  Hz,  $^3J(HH) = 8$  Hz,  $H^5$ ), 6.99 (dd, 1H,  $^3J(HH) = 9$  Hz,  $^3J(HH) = 8$  Hz,  $H^4$ ), 6.83 (d, 1H,  $^3J(HH) = 8$  Hz,  $H^6$ ), 3.09 (d, 1H,  $^2J(HH) = 9$  Hz,  $^2J(PtH) = 65$  Hz,  $CH_2^g$ ), 2.22 (d, 1H,  $^2J(HH) = 9$  Hz,  $^2J(PtH) = 106$  Hz,  $CH_2^h$ ), 1.47 (s, 9H,  $tBu$ ), 1.40 (s, 9H,  $tBu$ ), 1.30 (s, 3H, Me), 1.10 (s, 3H, Me);  $\delta(^{13}C)$  165.2, 164.6, 164.0, 155.6, 154.8, 154.7, 146.1, 134.2, 126.9, 126.3, 125.9, 125.7, 125.5, 124.8, 121.3, 121.2, 46.0, 36.2, 36.1, 32.3 ( $Me^a$ ), 31.4 ( $CH_2$ ), 31.2 ( $Me^b$ ), 30.7 (Me of  $tBu$ ), 30.6 (Me of  $tBu$ ).

4.4.  $[Pt(OH)_2(CH_2CMe_2C_6H_4)(phen^*)]$ , 7

To a solution of complex **2**, prepared *in situ* from complex **1** (0.082 g, 0.105 mmol) and ligand phen\* (0.050 g, 0.209 mmol) in acetone (5 mL), was added aqueous  $H_2O_2$  (30  $\mu$ L, 0.300 mmol) and methanol (2 mL) to give a clear yellow solution, which was layered with pentane (30 mL). Colorless block crystals of **7** were obtained after 2 days. After decanting the mother liquor, the crystals were washed with pentane and dried in vacuum. Yield: 0.076 g, 61%. Anal. Calcd. for  $C_{26}H_{30}N_2O_2Pt$ : C, 52.25; H, 5.06; N, 4.69. Found: C, 52.44; H, 5.10; N, 4.75%. NMR in  $CD_3OD$ :  $\delta(^1H)$  9.57 (s, 1H,  $H^{2a}$ ), 9.08 (s, 1H,  $H^{9a}$ ), 8.44 (d, 1H,  $^3J(HH) = 9$  Hz,  $H^{5a}$  or  $6a$ ), 8.40 (d, 1H,  $^3J(HH) = 9$  Hz,  $H^{5a}$  or  $6a$ ), 7.80 (d, 1H,  $^3J(HH) = 8$  Hz,  $^3J(PtH) = 19$  Hz,  $H^3$ ), 7.14 (t, 1H,  $^3J(HH) = 8$  Hz,  $H^5$ ), 7.10 (t, 1H,  $^3J(HH) = 8$  Hz,  $H^4$ ), 6.96 (d, 1H,  $^3J(HH) = 8$  Hz,  $H^6$ ), 3.88 (s, 2H,  $^2J(PtH) = 81$  Hz,  $CH_2$ ), 2.93 (s, 3H, Me), 2.91 (s, 3H, Me), 2.78 (s, 3H, Me), 2.72 (s, 3H, Me),

1.51 (s, 6H,  $Me_2$ );  $\delta(^{13}C)$  163.8, 150.0, 149.5, 146.7, 146.5, 144.9, 144.7, 133.9, 133.8, 130.2, 130.1, 129.6, 129.4, 125.4, 125.1, 124.1, 123.6, 123.3, 44.4 ( $CH_2$ ), 40.7, 32.6 (Me), 16.6 (Me), 16.3 (Me), 13.7 (Me), 13.6 (Me).

4.5.  $[PtCl(OH)(CH_2CMe_2C_6H_4)(phen^*)]$ , 8

To a sample of complex **2**, prepared *in situ* by reaction of complex **1** (0.097 g, 0.124 mmol) and ligand phen\* (0.059 g, 0.248 mmol) in  $CH_2Cl_2$  (10 mL), was added  $H_2O_2$  (30  $\mu$ L, 0.300 mmol) and methanol (3 mL) to give a clear solution. Upon slow evaporation at room temperature, colorless block crystals of complex **5** were obtained after 3 days. After decanting the mother liquor, the crystals were washed with pentane and dried in vacuo. Yield: 0.076 g, 50%. Anal. Calcd. for  $C_{26}H_{29}ClN_2OPt$ : C, 50.09; H, 4.74; N, 4.55. Found: C, 50.33; H, 4.80; N, 4.59%. NMR in  $CD_2Cl_2$ :  $\delta(^1H)$  9.52 (s, 1H,  $H^{2a}$ ), 9.00 (s, 1H,  $H^{9a}$ ), 8.34 (s, 1H,  $H^{5a}$  or  $6a$ ), 8.33 (s, 1H,  $H^{5a}$  or  $6a$ ), 7.71 (d, 1H,  $^3J(HH) = 7$  Hz,  $^3J(PtH) = 32$  Hz,  $H^3$ ), 7.13 (dd, 1H,  $^3J(HH) = 7$  Hz,  $^3J(HH) = 9$  Hz,  $H^4$ ), 7.08 (dd, 1H,  $^3J(HH) = 7$  Hz,  $^3J(HH) = 9$  Hz,  $H^5$ ), 6.92 (d, 1H,  $^3J(HH) = 7$  Hz,  $H^6$ ), 4.15 (d, 1H,  $^2J(HH) = 8$  Hz,  $^2J(PtH) = 80$  Hz,  $CH^a$ ), 3.94 (d, 1H,  $^2J(HH) = 8$  Hz,  $^2J(PtH) = 94$  Hz,  $CH^b$ ), 2.89 (s, 3H, Me), 2.88 (s, 3H, Me), 2.75 (s, 3H, Me), 2.69 (s, 3H, Me), 1.54 (s, 3H,  $Me^a$ ), 1.47 (s, 3H,  $Me^b$ ).

4.6.  $[Pt(OH)_2(CH_2CMe_2C_6H_4)(phen^*)](m-ClC_6H_4CO_2)_2$ , 9

To a sample of complex **2**, prepared *in situ* from complex **1** (0.100 g, 0.128 mmol) and ligand phen\* (0.060 g, 0.257 mmol) in acetone (5 mL), was added 3-chloroperbenzoic acid (0.115 g, 0.259 mmol) in acetone (2 mL). The solution was stirred for 1 h to give a white precipitate, which was separated by filtration, washed with acetone ( $2 \times 10$  mL) and pentane ( $2 \times 10$  mL) and dried under vacuum. Yield: 0.163 g, 70%. Anal. Calcd. for  $C_{40}H_{40}Cl_2N_2O_6Pt$ : C, 52.75; H, 4.43; N, 3.08. Found: C, 53.10; H, 4.44; N, 3.00%. NMR in  $CDCl_3$ :  $\delta(^1H)$  9.49 (s, 1H,  $^3J(PtH) = 14$  Hz,  $H^{2a}$ ), 9.05 (s, 1H,  $^3J(PtH) = 14$  Hz,  $H^{9a}$ ), 8.33 (d, 1H,  $^3J(HH) = 6$  Hz,  $H^{5a}$  or  $6a$ ), 8.32 (d, 1H,  $^3J(HH) = 6$  Hz,  $H^{5a}$  or  $6a$ ), 7.80 (s, 2H,  $H^{2b}$ ), 7.78 (d, 2H,  $^3J(HH) = 9$  Hz,  $H^{6b}$ ), 7.77 (d, 1H,  $^3J(HH) = 8$  Hz,  $H^3$ ), 7.48 (d, 2H,  $^3J(HH) = 8$  Hz,  $H^{4b}$ ), 7.36 (dd, 2H,  $^3J(HH) = 9$  Hz,  $8$  Hz,  $H^{5b}$ ), 7.18 (dd, 1H,  $^3J(HH) = 8$  Hz,  $^3J(HH) = 8$  Hz,  $H^4$ ), 7.15 (dd, 1H,  $^3J(HH) = 8$  Hz,  $^3J(HH) = 7$  Hz,  $H^5$ ), 7.00 (d, 1H,  $^3J(HH) = 7$  Hz,  $H^6$ ), 3.99 (s, 2H,  $^2J(PtH) = 74$  Hz,  $CH_2$ ), 2.85 (s, 3H, Me), 2.84 (s, 3H, Me), 2.70 (s, 3H, Me), 2.66 (s, 3H, Me), 1.53 (s, 6H,  $Me_2$ );  $\delta(^{13}C)$  170.5, 164.9, 151.6, 151.2, 149.1, 148.8, 146.2, 146.1, 137.3, 135.8, 135.6, 135.2, 132.7, 131.7, 131.3, 131.1, 130.8, 130.5, 130.2, 128.9, 127.8, 127.0, 125.9, 125.3, 125.0, 46.1, 44.4 ( $CH_2$ ), 33.7 (Me), 18.2 (Me), 18.0 (Me), 15.3 (Me), 15.2 (Me). Recrystallization from  $CH_2Cl_2$ /pentane gave the complex **9.10** ( $m-ClC_6H_4CO_2$ )<sub>3</sub>.

4.7.  $[PtCl(OOC(=O)C_6H_4-m-Cl)(CH_2CMe_2C_6H_4)(phen^*)]$ , 11

To a solution of 3-chloroperbenzoic acid (0.104 g, 0.600 mmol) in  $CH_2Cl_2$  (5 mL) was added a solution of complex **2** (0.200 mmol) in  $CH_2Cl_2$  (5 mL) to form a colorless solution. After 1 h, pentane (40 mL) was added to give an off-white precipitate, which was washed with diethyl ether ( $2 \times 10$  mL) and pentane ( $2 \times 10$  mL) and dried under vacuum, then recrystallized from  $CH_2Cl_2$ /pentane. Yield: 0.116 g, 25%. NMR in  $CD_3OD$ :  $\delta(^1H)$  9.51 (s, 1H,  $^3J(PtH) = 4$  Hz,  $H^{2a}$ ), 8.99 (s, 1H,  $^3J(PtH) = 7$  Hz,  $H^{9a}$ ), 8.31 (d, 1H,  $^3J(HH) = 9$  Hz,  $H^{5a,6a}$ ), 8.28 (d, 1H,  $^3J(HH) = 9$  Hz,  $H^{5a,6a}$ ), 7.89 (s, 1H,  $H^{2b}$ ), 7.84 (d, 1H,  $^3J(HH) = 8$  Hz,  $H^{4b}$ ), 7.71 (d, 1H,  $^3J(HH) = 7$  Hz,  $H^3$ ), 7.52 (d, 1H,  $^3J(HH) = 8$  Hz,  $H^{6b}$ ), 7.38 (t, 1H,  $^3J(HH) = 8$  Hz,  $H^{5b}$ ), 7.14 (t, 1H,  $^3J(HH) = 7$  Hz,  $H^4$ ), 7.09 (t, 1H,  $^3J(HH) = 7$  Hz,  $H^5$ ), 6.94 (d, 1H,  $^3J(HH) = 7$  Hz,  $H^6$ ), 4.18 (d, 1H,  $^2J(HH) = 7$  Hz,  $^2J(PtH) = 84$  Hz,  $CH_2$ ), 3.95 (d, 1H,  $^2J(HH) = 7$  Hz,  $^2J(PtH) = 80$  Hz,  $CH_2$ ), 2.86 (s, 3H, Me),

2.85 (s, 3H, Me), 2.74 (s, 3H, Me), 2.68 (s, 3H, Me), 1.54 (s, 3H, Me), 1.47 (s, 3H, Me);  $\delta(^{13}\text{C})$  168.5, 164.8, 150.7, 150.0, 147.6, 147.4, 145.5, 145.3, 135.0, 134.9, 134.8, 134.2, 133.2, 130.8, 130.6, 130.5, 130.4, 130.3, 129.3, 128.5, 126.7, 126.3, 125.5, 124.6, 124.3, 45.4, 43.2 (CH<sub>2</sub>), 33.9 (Me), 33.8 (Me), 18.5 (Me), 18.2 (Me), 15.4 (Me), 15.3 (Me).

### Supporting information

CCDC 1901263–1901269 contain the supplementary crystallographic data for the complexes. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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